UNIVERSITY OF PENNSYLVANIA

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WALLACE MORGAN McNABB

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

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INTRODUCTION

The determination of phosphoric acid by the precipitation of $MgNH_4PO_4$ and ignition to $Mg_2P_2O_7$ has been known for many years. As early as 1845 Fresenius[1] tells of the unjustified opinions given in chemical handbooks concerning the relative solubility of $MgNH_4PO_4$ which has been used in experiments for the determination of phosphoric acid. He determined the solubility of $MgNH_4PO_4$ in ammonia water, in ammonium chloride water and in water containing ammonium chloride and ammonia. From his experiments he concluded that the precipitate is sufficiently insoluble in ammonium chloride and ammonia to warrant its use as a method of determination. He states: "Pure sodium phosphate was dissolved in water and precipitated with the addition of magnesium sulphate, ammonium chloride and ammonium hydroxide, filtered, washed with ammonia water, dried and ignited." Kubel and Kissel[2] 1869, criticised Fresenius on the solubility of $MgNH_4PO_4$ in water containing free ammonia and magnesia mixture. They carried out the same experiments using magnesium sulphate, allowing the solution to stand twelve hours before filtering and obtained higher results. They also noted the danger of the formation of magnesium hydroxide and basic sulphate.

In 1871, Brunner[3] pointed out that the solution must not be precipitated by use of $MgSO_4$ while hot on account of the danger of throwing down $Mg(OH)_2$. Gibbs in 1873[4], determined magnesium as the pyrophosphate by making the precipitation of $MgNH_4PO_4$ in a boiling solution using microcosmic salt as the precipitant. After cooling ammonia was added and the process continued in the usual way.

From a number of experiments carried out in the determination of P_2O_5 from alkaline phosphates free from sulphates, Gooch[5] in 1879 claimed that accuracy is more easily obtained by adding

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[1] Fresenius. *Annalen der Chemie und Pharmacie* 1845, p. 109.
[2] Kubel and Kissel. *Zeit. für Anal. Chem.* 1869, Vol. 8, p. 125.
[3] Brunner. *Zeit. für Anal. Chem.* 1871, Vol. 11, p. 30.
[4] Gibbs, W. *Amer. Jour. Science* 1873, (Silliman) (3), Vol. 5, p. 114.
[5] Gooch. *Amer. Chem. Jour.* 1879, Vol. 1.

ammonia in slight excess to the phosphate. Then to this solution he added an excess of magnesia mixture made from the chloride containing no free ammonia. After the precipitate settled, ammonia water was added until a strong odor prevailed. He also showed[6] that consistent results cannot be obtained by carrying out the precipitation in the cold.

Brookman[7] in 1882, claims that the best and most accurate results were obtained by dissolving the precipitate of $MgNH_4PO_4$ off the filter paper with dilute nitric acid into a weighed porcelain basin, evaporating and igniting.

Neubauer[8] in 1894, was one of the first to show the differences in the precipitation of $MgNH_4PO_4$ due to variation of three conditions: first, if the precipitate is formed in a neutral or ammoniacal solution and does not contain an excess of magnesia mixture, the precipitate of $MgNH_4PO_4$ is contaminated with $Mg(NH_4)_4(PO_4)_2$ which on ignition goes to the metaphosphate and finally to the pyrophosphate with a loss of some P_2O_5. The condition tends to give low results. Second, if the precipitate is formed in the presence of an excess of magnesia mixture and during its formation an excess of ammonia is never present, a normal precipitate is obtained and is free from secondary products. This condition would give the most accurate results. Third, if the precipitate is formed in the presence of an excess of magnesia mixture and ammonia is also present in excess, the precipitate always contains some $Mg_3(PO_4)_2$. This condition would give high results.

Neubauer recommends a method in which the precipitation can be carried out according to the first condition and to the weight of $Mg_2P_2O_7$ obtained, a correction is added to compensate for the loss by ignition.

It is evident from the study of the precipitation of $MgNH_4PO_4$ by Neubauer[9] in 1896, that it is very difficult to obtain pure magnesium ammonium phosphate in a cold solution. Sometimes the precipitate is contaminated with $Mg_3(PO_4)_2$ and sometimes with $Mg(NH_4)_4(PO_4)_2$.

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[6] Gooch. *Zeit. Anorg. Chem.* 1899, Vol. 20, p. 135.
[7] Brookman, K. *Repert. Anal. Chem.* 1882, Vol. 2, p. 297.
[8] Neubauer, H. *Zeit. für Anal. Chem.* 1894, Vol. 33, p. 362.
[9] Neubauer, H. *Zeit. Angew. Chem.* 1896, p. 439.

A study of the precipitation of $MgNH_4PO_4$ was carried out by Mahon[10] in 1898 with systematic variations of the conditions. Gooch and Austen[11] 1899, recommended that when an excess of ammonium chloride and more magnesium salt than twice the amount theoretically necessary is present, it is safe to decant the supernatant liquid through the filter from the precipitate, dissolve the precipitate in a little hydrochloric acid and reprecipitate with dilute ammonia, wash with weak ammonia water and ignite in the usual way.

Järvinen[12], [13] in 1904 and 1905 recommended that the precipitation of $MgNH_4PO_4$ be carried out in a hot solution, a pure crystalline precipitate of $MgNH_4PO_4.6\ H_2O$ being obtained. If the precipitation is carried out according to Schmitz[14] 1906, in which 2.5 per cent ammonium hydroxide is added slowly to a hot solution of phosphoric acid containing magnesia mixture and ammonium chloride, a pure crystalline precipitate of $MgNH_4PO_4.6\ H_2O$ is obtained. Jörgensen[15] 1906, also recommended precipitation in a hot solution. Jones[16] 1916, stated that the conversion of $MgNH_4PO_4.6\ H_2O$ into $Mg_2P_2O_7$ is a superfluous operation. He recommended that the crystalline precipitate be dried at room temperature or at 40° C. and weighed.

In a comparative systematic study of different methods of precipitation of $MgNH_4PO_4$ Balareff[17] 1917, found that the older cold method of precipitation of Neubauer and the hot methods of Schmitz, Jörgensen and Järvinen gave equally satisfactory results providing the precipitation took place in a pure aqueous solution. In the presence of alkaline cations high results were obtained, the effect being smaller when the precipitation was carried out at high temperatures. Sulphate ions had the same effect as the alkaline ions. He recommended that rapid precipitation at a high temperature was best for accurate results.

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[10] Mahon. *Jour. Amer. Chem. Soc.* 1898, Vol. 20.
[11] Gooch, F. A. and Austin, M. *Chem. Centr.* 1899, Vol. 1 (15), p. 902.
[12] Järvinen, K. K. *Zeit. Anal. Chem.* 1904, Vol. 43, p. 279.
[13] Järvinen, K. K. *Zeit. Anal. Chem.* 1905, Vol. 44, p. 333.
[14] Schmitz, B. *Zeit. Anal. Chem.* 1906, Vol. 45, p. 512.
[15] Jörgensen, G. *Zeit. Anal. Chem.* 1906, Vol. 45, p. 278.
[16] Jones, W. *Jour. Biol. Chem.* 1916, Vol. 25, p. 87.
[17] Balareff, D. *Zeit. Anorg. Allgem. Chem.* 1917, Vol. 101, p. 229.

A study of the various methods for the precipitation of $MgNH_4PO_4$ by Karaoglanow[18] in 1918, indicated that the results were dependent on the temperature of precipitation, time for complete precipitation and proportions of magnesia mixture and ammonium chloride used. In most cases however, the differences were small, although consistent results were obtained with wide variations of conditions according to the Schmitz method in which the precipitation was carried out in a hot solution. Balareff[19] 1919, found that a pure crystalline $MgNH_4PO_4$ can be formed only under very special conditions. If too small an amount of ammonium chloride was used and the solution was not stirred during the precipitation the results were too high. The use of fixed alkaline phosphate in place of phosphoric acid caused high results on account of the precipitation of fixed alkaline magnesium phosphate.

According to Winkler[20] 1919, the presence of sodium and potassium chloride in the solution caused high results in the determination of P_2O_5 as $MgNH_4PO_4$. Desbourdeux[21] 1920, indicated that with ammonium nitrate the precipitation was almost complete when hot, complete when cold, using small amounts of magnesia mixture. When ammonium chloride, potassium chloride or potassium sulphate was used, complete precipitation took place in the cold. The presence of ammonium sulphate caused incomplete precipitation in all cases. Precipitation was complete in the presence of sodium nitrate, sodium chloride or sodium sulphate; but with the same potassium salts it was also satisfactory in warm solutions.

In a criticism given by Balareff[22] 1921, certain apparent contradictions concerning the various methods used in the precipitation of $MgNH_4PO_4$ were explained. He concluded that (1) precipitation of $MgNH_4PO_4$ in the cold should be discarded. Accuracy could be obtained only when the concentration of the alkali cations and the sulphate anions and the quantity

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[18] Karaoglanow, Z. *Zeit. Anal. Chem.* 1918, Vol. 57, p. 497.
[19] Balareff, D. *Zeit. Anorg. Allgem. Chem.* 1919, Vol. 106, p. 268.
[20] Winkler, L. W. *Zeit. Angew. Chem.* 1919, Vol. 32, p. 99.
[21] Desbourdeux, L. *Bull. Sci. Pharmacol.* 1920, Vol. 27, p. 225 and p. 300.
[22] Balareff, D. *Zeit. Anorg. Allgem. Chem.* 1921, Vol. 117, p. 91.

of ammonium chloride and ammonia vary within narrow limits. (2) Methods used in double precipitations that were carried out gave good results only when the precipitate was dissolved in a liberal quantity of hydrochloric acid and a second precipitation made by the rapid addition of 10 per cent ammonia. (3) Jörgensen's method was inaccurate. (4) The results of Järvinen's method were dependent on the quantity of alkali cations present. (5) All methods given above were compensation methods. (6) The Schmitz method was found to be the most accurate providing the conditions were carefully defined.

The latter method, used in the experimental part of this paper is as follows: Schmitz[23] 1924, found most accurate results were obtained by the addition of ammonium acetate to the solution. To the phosphoric acid solution 30 cc. of magnesia mixture and 5 grams of ammonium acetate were added, after adding several drops of phenolphthalein indicator the solution was heated to nearly boiling and with rapid stirring 2.5 per cent ammonium hydroxide added drop by drop until a pink color was obtained. On cooling strong ammonium hydroxide was added and the solution filtered. The presence of ammonium acetate decreased the solubility of $MgNH_4PO_4$ and prevented the formation of secondary products which so often contaminate the precipitate.

McCandless and Burton[24] 1924, gave a quick and accurate method for the precipitation of $MgNH_4PO_4$ in the cold. The magnesia mixture and ammonium hydroxide were added to the nearly neutralized phosphoric acid solution. The solution was filtered, washed with 2.5 per cent ammonium hydroxide and then with a strong solution of ammonium nitrate. Caro and Larison[25] 1925 using the same method, obtained low results. Jörgensen[26] 1925, and also Neubauer (Inaug. Dissert. 1893) got high results. It was Jörgensen's belief that precipitation from a cold solution was too readily influenced by slight variations in procedure and for this reason he gave up the method. He also

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[23] Schmitz, B. *Zeit. Anal. Chem.* 1924, Vol. 65, p. 46.
[24] McCandless and Burton, J. *Ind. Eng. Chem.* 1924, Vol. 16, p. 1267.
[25] Caro, R. J. and Larison, E. C. *Ind. Eng. Chem.* 1925, Vol. 17, p. 261.
[26] Jörgensen, G. *Zeit. Anal. Chem.* 1925, Vol. 66, p. 209 and *The Analyst*, Vol. 51, No. 599, p. 61.

stated that it has been abandoned in England (B. Dyer, "Fertilizers" in Thorp's Dictionary of Applied Chemistry, 1922, Vol. 3.) and in Germany (Verein Deutscher Düngerfabrikanten. Methoden zur Untersuchungen der Kunstdüngermittel, 1916).

A review of the literature indicates that uncertainty exists in the determination of P_2O_5 by the precipitation of $MgNH_4PO_4$ which is finally converted to $Mg_2P_2O_7$ by ignition; and in spite of the large amount of work that has been done, there is still need for further investigation in this field.

EXPERIMENTAL RESULTS

Reagents

1. A 1 per cent solution of disodium hydrogen phosphate.
2. A 0.5 per cent and a 2 per cent solution of monopotassium hydrogen phosphate.
3. Neutral magnesia mixture. (55 grams of magnesium chloride and 105 grams of ammonium chloride were made up to a liter and filtered, the filtrate was made weakly acid with 1:10 hydrochloric using methyl orange as an indicator.)
4. A 10 per cent and a 20 per cent solution of ammonium acetate.
5. A 2.5 per cent solution of ammonium hydroxide.
6. A 1:10 hydrochloric acid solution.
7. A 1:3 nitric acid solution.
8. Phenolphthalein solution (1 gram to 100 cc. of alcohol).

Weights

All weighings were made with a set of weights calibrated by the Richards method[1].

The factor used in calculating the P_2O_5 from the weight of $Mg_2P_2O_7$ obtained was 0.63788.

Some preliminary experiments indicated that it might be possible to make a complete precipitation of $MgNH_4PO_4$ in cold solutions. Using a solution of disodium hydrogen phosphate, a number of qualitative precipitations were made in the cold with variations in the concentration of magnesia mixture, ammonium chloride, ammonium hydroxide and time for precipitation, keeping the temperature below 10° C. Without washing the precipitate free from chlorides the filtrate always gave a positive test for phosphate which showed incomplete precipitation in the cold. A number of precipitations were made with systematic variations in the temperature from 5° C. to 60° C. just before filtering, everything else remaining constant. All

[1] Richards. *Jour. Amer. Chem. Soc.* 1900, Vol. 22, p. 144.

filtrates gave a positive test for phosphate. With variations in the concentration of ammonium hydroxide a few precipitations were made at boiling temperature then cooled with ice to room temperature and filtered; filtrates in each case gave a positive test for phosphate.

In all cases each filtrate was allowed to stand not less than twenty-four hours. Any trace of phosphate present could be recognized by rubbing the bottom of the beaker with a stirring rod. This test was found to be entirely satisfactory. Several filtrates which gave a negative test for phosphate were evaporated to dryness and ignited in a platinum dish until all ammonia salts were driven off, the residue dissolved in a few cubic centimeters of dilute hydrochloric acid and a few cubic centimeters of magnesia mixture added, then made alkaline with ammonium hydroxide and heated with vigorous stirring, rubbing the sides of the beaker with a glass rod. These did not give a test for phosphate. Several filtrates which gave a positive test for phosphate by the former method were carried through the same operation in a platinum dish and they gave a positive test for phosphate. Precipitation in the cold seemed to offer so little prospect of success that efforts in this direction were discontinued.

After completing a number of qualitative experiments according to the method of Schmitz[2] in boiling hot solution and according to another of his methods[3] in which he uses ammonium acetate, which tends to decrease the solubility of the magnesium ammonium phosphate formed and regulates the precipitation in such a way that secondary products do not form so easily; it was decided to use the ammonium acetate method for the precipitation of magnesium ammonium phosphate in quantitative experiments. Since the complete removal of such precipitates from a beaker is often tedious and uncertain, it was thought desirable to attempt to combine this method of precipitation with the apparently more reliable method of handling the precipitate, consisting in dissolving it from off the filter paper and

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[2] Schmitz, B. *Zeit. Anal. Chem.* 1906, Vol. 45, p. 512.
[3] Schmitz, B. *Zeit. Anal. Chem.* 1924, Vol. 65, p. 46.

beaker walls with dilute nitric acid, collecting in a tared crucible, evaporating the solution to dryness, igniting and weighing.

After the precipitations were made in a hot solution of magnesia mixture, ammonium acetate and 2.5 per cent ammonium hydroxide was added drop by drop until a faint pink color was obtained (using phenolphthalein as an indicator); the solution was allowed to cool, one-fifth of its volume of strong ammonium hydroxide added and filtered. The method of Brookman[4] was used to complete the determination. This method is used at the present time by some chemists and is considered as being most accurate. The method as given by Brookman and used today recommends that the magnesium ammonium phosphate after being well washed upon the filter, be dissolved in nitric acid together with the particles clinging to the sides of the beaker, and the solution be then poured directly into a weighed porcelain crucible, evaporated to dryness and ignited. In this manner a loss of the precipitate, which only too often occurs in the methods hitherto used, is avoided. Reduction through carbon of the filter paper is eliminated. The presence of filter ash and tedious manipulation are avoided. The results are very exact compared with those obtained by the customary method. The values are slightly higher. It may be mentioned that platinum crucibles are now used in place of porcelain. The author in all analyses used 1:3 nitric acid in dissolving the precipitate, and it was found that adding a few drops of ammonium hydroxide before evaporating made heating just before ignition easier to control.

Results of quantitative experiments carried out according to the combined Schmitz and Brookman method are given in Table I. In each analysis the ignition, with a Bunsen burner flame, was continued twenty minutes and no change in weight was shown on a half hour further ignition.

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[4] Brookman, K. *Repert. Anal. Chem.* 1882, Vol. 2, p. 297.

TABLE I

ANALYSES BY A COMBINED SCHMITZ AND BROOKMAN METHOD USING A STOCK SOLUTION OF Na_2HPO_4

Na_2HPO_4 cc.	H_2O cc.	$NH_4C_2H_3O_2$ 10% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight. gms.	P_2O_5 calcu. gms.	Filtrate Test
PRECIPITATE WASHED WITH 1:3 NH_4OH SOLUTION							
50	50	50	30	35	0.46823	0.29868	+
50	50	50	30	35	0.46741	0.29697	+
50	50	50	30	35	0.46885	0.29908	+
50	50	50	30	35	0.46891	0.29911	+
50	50	50	30	35	0.46862	0.29892	+
PRECIPITATE WASHED WITH 2.5% NH_4OH SOLUTION							
50	50	50	30	35	0.46845	0.29882	+
50	50	50	30	35	0.46862	0.29893	+
50	50	50	30	35	0.46922	0.29972	+
50	50	50	30	35	0.46861	0.29892	+
50	50	50	30	35	0.46812	0.29861	+
50	50	50	30	35	0.47002	0.29982	+

Since a strong positive test for phosphoric acid was always obtained in the filtrate in using the disodium hydrogen phosphate, probably due to the presence of sodium chloride which tends to dissolve the magnesium ammonium phosphate, the monopotassium salt was substituted. The results of analyses made using a stock solution of monopotassium hydrogen phosphate are given in Table II.

TABLE II

ANALYSES BY A COMBINED SCHMITZ AND BROOKMAN METHOD USING A STOCK SOLUTION OF KH_2PO_4 AND IGNITING THE PRECIPITATE OVER A BUNSEN BURNER

KH_2PO_4 cc.	H_2O cc.	$NH_4C_2H_3O_2$ 10% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	P_2O_5 calcu. gms.	Filtrate Test
PRECIPITATE WASHED WITH 1:3 NH_4OH SOLUTION							
50	50	50	30	35	0.17915	0.11427	+
50	50	50	30	35	0.18070	0.11526	—
50	50	50	30	35	0.18062	0.11521	—
50	50	50	30	35	0.18062	0.11521	—
50	50	50	30	35	0.18052	0.11515	—
50	50	50	30	35	0.18032	0.11502	trace
50	50	50	30	35	0.18042	0.11509	trace
PRECIPITATE WASHED WITH 1:4 NH_4OH SOLUTION							
50	50	50	30	35	0.17942	0.11445	+
50	50	50	30	35	0.18002	0.11483	+
PRECIPITATE WASHED WITH 2.5% NH_4OH SOLUTION							
50	50	50	30	35	0.18032	0.11502	trace
50	50	50	30	35	0.17902	0.11419	+
50	50	50	30	35	0.18022	0.11469	trace
50	50	50	30	35	0.18082	0.11535	—

According to Gooch[5] it is necessary only to heat the precipitate to full red heat. As ignitions are usually carried out between 900° and 1000° C. and, since the ignitions in Tables I and II were carried out at about 750° C., it was decided to follow the customary method and ignite thereafter at white heat. Determination of the temperature produced by a Meker burner in a platinum crucible was found to be between 950° and 1000° C.

When between 0.1 and 0.2 gram of precipitated magnesium ammonium phosphate was heated in a platinum crucible at first gently and finally ignited over a Meker burner, a loss in weight as given in Table III was noted. Since the platinum crucible, when heated alone the same length of time and under the same conditions did not change weight, it is indicated that the burner gases penetrate the platinum crucible and tend to reduce the ignited product.

By means of a pyrometer, the temperature was determined in a platinum crucible supported on a platinum foil in the bottom of a porcelain crucible and heated with a Meker burner. The temperature in the platinum crucible with the lid on was found to be about 900° C. This arrangement prevented reduction by the burner gases and was subsequently used in igniting to constant weight.

Analyses, given in Table IV, of a stock solution of monopotassium hydrogen phosphate were then made according to the combined Schmitz and Brookman method.

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[5] Gooch, F. A. *Representative Procedures in Quantitative Chemical Analysis*, p. 84, John Wiley & Sons, New York, 1916.

TABLE III

EXPERIMENTS SHOWING REDUCTION OF PRECIPITATE DUE TO PENETRATION OF BURNER GAS

	Time of ignition with Meker burner directly Minutes	Weight of platinum crucible with precipitate Grams
1.	1st 30 min. period	20.3673
	2nd 30 " "	20.3670
	3rd 30 " "	20.3666
2.	1st 30 min. period	20.7599
	2nd 30 " "	20.7595
	3rd 30 " "	20.7585
	4th 30 " "	20.7582
3.	1st 30 min. period	20.7668
	2nd 30 " "	20.7562
	3rd 30 " "	20.7558
4.	1st 5 min. period	20.7594
	2nd 5 " "	20.7593
	3rd 5 " "	20.7592
	4th 5 " "	20.7591
	5th 5 " "	20.7589
	6th 5 " "	20.7587
5.	1st 5 min. period	20.7588
	2nd 5 " "	20.7586
	Platinum crucible placed in porcelain crucible containing platinum foil in bottom	
	3rd 5 min. period	20.7586
	4th 10 " "	20.7586
	Meker burner directly	
	5th 5 min. period	20.7585

TABLE IV

ANALYSES BY THE COMBINED SCHMITZ AND BROOKMAN METHOD OF A STOCK SOLUTION OF KH_2PO_4, IGNITING WITH A MEKER BURNER AND USING AN OUTER PORCELAIN CRUCIBLE FOR PROTECTION

KH_2PO_4 cc.	H_2O cc.	$NH_4C_2H_3O_2$ 10% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	P_2O_5 calcu. gms.	Filtrate Test
10	—	50	30	20	0.10067	0.06421	—
10	—	50	30	20	0.10067	0.06421	—
10	—	50	30	20	0.10060	0.06417	—
10	—	50	30	20	0.10070	0.06422	—
10	—	50	30	20	0.10060	0.06417	—
10	—	50	30	20	0.10057	0.06415	—
10	—	50	30	20	0.10117	0.06453	—
10	—	50	30	20	0.10107	0.06447	—
10	—	50	30	20	0.10077	0.06428	—
10	—	50	30	20	0.10157	0.06479	—
10	—	50	30	20	0.10190	0.06499	—
10	—	50	30	20	0.10111	0.06449	—
10	—	50	30	20	0.10163	0.06483	—
10	—	50	30	20	0.10167	0.06485	—

PRECIPITATE WASHED WITH 2.5% NH_4OH SOLUTION

Examination of the results in Table IV indicated that while the precipitation was apparently complete in each instance, some variable, either alteration of the stock solution or change due to dissolving in nitric acid before ignition, was responsible for lack of concordance in this series. Analyses, using the same procedure, were then made of weighed samples of the monopotassium hydrogen phosphate after recrystallizing and drying in a dessicator over concentrated sulphuric acid. The results given in Table V were obtained.

TABLE V

ANALYSES BY THE COMBINED SCHMITZ AND BROOKMAN METHOD USING A WEIGHED SAMPLE OF RECRYSTALLIZED KH_2PO_4

KH_2PO_4 weight gms.	H_2O cc.	$NH_4C_2H_3O_2$ 10% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	$Mg_2P_2O_7$ theor. gms.	$Mg_2P_2O_7$ differ- ence	Filtrate Test
0.2000	5	50	30	20	0.16121	0.16357	0.00236	—
"	5	50	30	20	0.15921	"	0.00436	—
"	5	50	30	20	0.16221	"	0.00136	—
"	5	50	30	20	0.16071	"	0.00286	—
Average					0.16083	0.16357	0.00273	

PRECIPITATE WASHED WITH 1:3 NH_4OH

After completing the analyses of the recrystallized salt and finding the large errors compared to the theoretical, it seemed possible that a loss might be due to the reaction taking place on ignition. According to Karaoglanow and Dimitrow,[6] when magnesium pyrophosphate is dissolved in nitric acid, evaporated and ignited, a loss of phosphorus pentoxide occurs. The loss as stated in the reference is probably due to the following reaction:

$$Mg_2P_2O_7 + 4\ HNO_3 = H_4P_2O_7 + 2\ Mg(NO_3)_2.$$

$H_4P_2O_7$ in acid solution changes to the orthophosphoric acid H_3PO_4, and this reacting with magnesium nitrate is probably a reversible reaction:

$$H_3PO_4 + Mg(NO_3)_2 <> MgHPO_4 + 2\ HNO_3$$

which on ignition gives a loss of P_2O_5.

Since a loss of phosphorus pentoxide occurs by dissolving magnesium pyrophosphate in nitric acid, evaporating and igniting; it was thought that the same reaction probably takes place when magnesium ammonium phosphate is dissolved in nitric acid, evaporated and ignited, because magnesium nitrate and phosphoric acid would be found reacting in the solution according to the following equation:

$$MgNH_4PO_4 + 3\ HNO_3 = Mg(NO_3)_2 + H_3PO_4 + NH_4NO_3$$
$$Mg(NO_3)_2 + H_3PO_4 = MgHPO_4 + 2\ HNO_3.$$

If this is the case then there is a loss of P_2O_5 when the residue is ignited, and in order to determine any loss of P_2O_5 the following qualitative experiments were carried out.

(1) About 0.4000 gram of recrystallized monopotassium hydrogen phosphate was dissolved in a small amount of water, several drops of dilute hydrochloric acid added, then 30 cc. of magnesia mixture and 50 cc. of 10 per cent ammonium acetate solution. After adding 2 drops of phenolphthalein indicator the solution was heated to boiling and 2.5 per cent ammonium hydroxide added drop by drop while stirring until a faint pink color was observed. After the solution was allowed to cool and one-fifth its volume of strong ammonium hydroxide added, the precipitate was filtered and well washed with 2.5 per cent ammonium hydroxide. The precipitate of magnesium ammonium

[6] Karaoglanow, Z. and Dimitrow, P. *Zeit Anal. Chem.* 1918, Vol. 57.

phosphate was then dissolved off the filter paper with warm 1:3 nitric acid and caught in a platinum crucible. The solution was evaporated on a water bath to a syrupy liquid, transferred to a sand bath and heated for about six hours with a low flame, gradually increased to full flame after which direct heat was applied very slowly with a Bunsen burner until red heat was obtained. During the operation of heating with the direct flame of the Bunsen burner, a watch crystal was placed over the top of the platinum crucible and a white coating formed on the under surface of the glass. Every fifteen minutes this coating was washed off the under surface of the glass into ammonium molybdate solution containing dilute nitric acid and ammonium nitrate. A yellow color appeared in the molybdic acid solution whereas a blank gave no test. On standing overnight the yellow increased in intensity, but the blank remained colorless.

(2) Experiment number 1 was repeated, a variation being made in the final heating. Instead of igniting by direct heat the platinum crucible was placed in a porcelain crucible and ignited with a Bunsen burner. The coating formed on the watch glass gave a yellow color in the molybdic acid solution compared to the blank.

(3) Experiment number 1 was again repeated with a second variation. After dissolving the precipitate of magnesium ammonium phosphate in warm 1:3 nitric acid, the solution in the platinum crucible was made alkaline with ammonium hydroxide then evaporated and ignited. No yellow color was obtained in the molybdic acid solution compared to a blank.

(4) Experiment number 3 was repeated with a variation in heating. The ignition was carried out in the platinum crucible placed in a porcelain crucible and strongly heated with a Bunsen burner. No yellow color was obtained in the molybdic acid solution compared to a blank.

(5) Experiments number 1 and 3 were again repeated and during the ignition a platinum dish was placed over the platinum crucible which in turn was placed in a porcelain crucible. The platinum dish was kept supplied with ice water during the ignition, which in this case was carried out with a Meker burner. Number 1 gave a yellow color while number 3 did not give a yellow color in the molybdic acid solution. Number 3 was

then heated again with a blast lamp for twenty minutes, but no yellow color could be obtained in the molybdic acid solution compared to a blank.

The results of these qualitative experiments very definitely prove that there is a loss of P_2O_5 in dissolving the magnesium ammonium phosphate in nitric acid and evaporating and igniting; but when the solution is made alkaline with ammonium hydroxide before evaporating and igniting there is no loss of the phosphorus pentoxide.

After having discovered through qualitative tests that a loss of phosphorus pentoxide takes place in dissolving magnesium ammonium phosphate in nitric acid, evaporating and igniting; and likewise having found that the addition of ammonium hydroxide to the dissolved magnesium phosphate prevents volatilization of phosphorus pentoxide on ignition, the quantitative experiments were resumed.

The reagents were purified as follows:

Monopotassium hydrogen phosphate of good grade was recrystallized in a platinum dish, filtered, centrifuged and dried over sulphuric acid. Magnesium chloride of high quality was recrystallized, filtered and well centrifuged.

Ammonium acetate was recrystallized, filtered and well centrifuged.

Ammonium chloride was dissolved to a saturated solution, boiled with ammonium hydroxide, filtered, cooled with ice, saturated with hydrogen chloride gas, filtered and well centrifuged, after which it was dried in an oven below the point of sublimation for several hours.

Ammonium hydroxide was redistilled to 15 per cent.

Nitric acid was redistilled.

This series of experiments, the results of which are given in Table VI, were carried out to show quantitatively that the presence of ammonium hydroxide in the dissolved magnesium ammonium phosphate prevents the volatilization of phosphorus pentoxide. We know that in dissolving magnesium pyrophosphate in nitric acid it changes to the orthophosphoric acid. According to the following reaction:

$Mg_2P_2O_7 + 5\ HNO_3 = H_4P_2O_7 + 2\ Mg(NO_3)_2 + HNO_3$ and
$MgNH_4PO_4 + 4\ HNO_3 = Mg(NO_3)_2 + NH_4NO_3 + H_3PO_4 + HNO_3$.

The only difference in the two reactions after the addition of the ammonium hydroxide to the dissolved $Mg_2P_2O_7$ and $MgNH_4PO_4$, is that the latter would contain more ammonium nitrate than the former; and this small amount of ammonium nitrate should not differently affect the evaporation and ignition of the products formed by the two reactions. For this reason the quantitative experiments were first carried out with magnesium pyrophosphate.

Two methods of precipitation of magnesium ammonium phosphate were used: one according to the method given in Treadwell and Hall, pages 434–435,[7] using ammonium chloride, and the other according to the method of Schmitz[8] using ammonium acetate instead of ammonium chloride. After the precipitates were well washed with 2.5 per cent ammonium hydroxide, they were transferred to a weighed platinum crucible and ignited between 900° and 1000° C. to constant weight. This ignited product, $Mg_2P_2O_7$, was then dissolved in warm 1:3 HNO_3, made alkaline with NH_4OH, evaporated and again ignited to constant weight.

It is to be noted in Table VI that when the evaporation is carried out after making alkaline with ammonium hydroxide there is no marked change in weight; but when the solution is not made alkaline before evaporation, but allowed to remain acid, there is a marked loss after the evaporation and ignition. The last part of analysis 4 in Table VI shows that loss does not occur in the evaporation, but during the ignition.

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[7] Treadwell and Hall. *Analytical Chemistry*, Vol. 2, pp. 434, 435, 1919. Fifth Edition. John Wiley & Sons, Inc., New York.
[8] Schmitz, B. *Zeit. Anal. Chem.* 1924, Vol. 65, p. 46.

TABLE VI

COMPARATIVE ANALYSES SHOWING LOSS OF P_2O_5 BY VOLATILIZATION WHEN THE PRECIPITATE IS DISSOLVED IN HNO_3, BUT THAT ADDITION OF NH_4OH PREVENTS THIS LOSS

	Crucible empty gms.	Crucible with ignited product gms.	Time of ignition min.	$Mg_2P_2O_7$ formed gms.
(1) $MgNH_4PO_4$ ignited to $Mg_2P_2O_7$.	20.65226	20.83303	1st 15	0.18077
		20.83299	2nd 15	0.18064
		20.83276	3rd 15	0.18050
		20.83278	4th 15	0.18052
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, NH_4OH added, evaporated in crucible and ignited.		20.83307	1st 15	0.18081
		20.83286	2nd 15	0.18060
		20.83283	3rd 15	0.18057
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, evaporated and ignited.		20.83010	1st 15	0.17784
		20.83010	2nd 15	0.17784
Ignited with direct heat of Meker burner.		20.82957	1st 15	0.17731
Ignited again with protected crucible.		20.87954	1st 15	0.17730
(2) $MgNH_4PO_4$ ignited to $Mg_2P_2O_7$.	21.10796	21.29781	1st 15	0.18985
		21.29770	2nd 15	0.18974
		21.29763	3rd 15	0.18967
		21.29765	4th 15	0.18969
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, NH_4OH added, evaporated in crucible and ignited.		21.29830	1st 15	0.19034
		21.29799	2nd 15	0.19003
		21.29781	3rd 15	0.18985
		21.29779	4th 15	0.18983

	Crucible empty gms.	Crucible with ignited product gms.	Time of ignition min.	$Mg_2P_2O_7$ formed gms.
(3) $MgNH_4PO_4$ ignited to $Mg_2P_2O_7$.	20.65003	20.91076	1st 15	0.26073
		20.91067	2nd 15	0.26064
		20.91065	3rd 15	0.26062
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, NH_4OH added, evaporated in crucible and ignited.		20.91073	1st 15	0.26070
		20.91063	2nd 15	0.26060
		20.91060	3rd 15	0.26057
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, evaporated and ignited.		20.90646	1st 15	0.25643
		20.90646	2nd 15	0.25643
(4) $MgNH_4PO_4$ ignited to $Mg_2P_2O_7$.	21.10796	21.48011	1st 15	0.37215
		21.47986	2nd 15	0.37190
		21.47988	3rd 15	0.37192
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, NH_4OH added, evaporated in crucible and ignited.		21.48012	1st 15	0.37216
		21.48000	2nd 15	0.37294
		21.47993	3rd 15	0.37197
		21.47992	4th 15	0.37196
$Mg_2P_2O_7$ dissolved in 1:3 HNO_3, evaporated to a syrupy liquid, diluted with water, NH_4OH added, evaporated, ignited.		21.48015	1st 15	0.37219
		21.47990	2nd 15	0.37194
		21.47984	3rd 15	0.37188

After having shown in the preceding qualitative and quantitative experiments that there is a loss when magnesium ammonium phosphate is dissolved in nitric acid and evaporated and ignited, but when the solution is made alkaline with ammonium hydroxide before evaporating and igniting there is no loss; a number of comparative analyses by the author's method and the nitric acid method were made showing the errors as calculated against theoretical. The results are given in Tables VIIa and VIIb respectively.

The following procedure was used for the rapid and complete precipitation of the phosphate in a pure crystalline state. The weighed samples of monopotassium hydrogen phosphate were transferred to a small beaker and dissolved in a small amount of water. To this solution was added several drops of dilute 1:10 hydrochloric acid, then 25 cc. of a 20 per cent solution of ammonium acetate and 30 cc. of magnesia mixture. After heating the solution nearly to boiling, several drops of phenolphthalein indicator were added and 2.5 per cent ammonium hydroxide drop by drop with constant stirring until a red color appeared. (If a faint turbidity appears at the beginning of the precipitation, the addition of ammonium hydroxide is discontinued and the solution vigorously stirred until the turbidity disappears and the precipitate becomes crystalline, which should result in about one-half minute.)

The solution was allowed to stand until completely cooled, then about one-fifth its volume of concentrated ammonium hydroxide added, stirred vigorously, allowed to stand a few minutes and then filtered. The precipitate was well washed in the beaker with 2.5 per cent ammonium hydroxide and poured onto the filter paper. After drawing the excess of ammonium hydroxide out of the precipitate by means of suction, a weighed platinum crucible was placed under the filter and a hole punched in the filter paper. Several drops of warm 1:3 nitric acid in a few cubic centimeters of water was used to dissolve the precipitate clinging to the sides of the beaker and this was used to wash most of the precipitate on the filter paper down into the crucible. The remaining part on the filter can easily be washed into the crucible by means of a wash bottle

throwing a fine stream. If any particles persist in clinging to the paper a drop or two of nitric acid can be used. (It was found best to use as small an amount of nitric acid as possible as this prevents the formation of an excess of ammonium nitrate, making the final heating much easier to carry out.)

Ammonium hydroxide was then added to the contents of the platinum crucible until a strong odor of NH_3 was obtained, and the crucible placed in a porcelain crucible on a steam bath protected from dust by means of an inverted funnel with a test tube over the top. After evaporating to dryness, the precipitate was heated gently at first on a ring burner and finally to red heat. The crucible was transferred to a porcelain crucible containing a platinum foil in the bottom and heated for fifteen minutes with a Meker burner at about 900° C. All ignitions were conducted for fifteen minutes, followed by ignitions for twenty minute periods until constant weight was attained.

TABLE VII-A

ANALYSES MADE BY THE AUTHOR'S METHOD IN WHICH NH_4OH IS ADDED TO THE CONTENTS OF THE CRUCIBLE BEFORE EVAPORATING AND IGNITING

H_2O cc.	$NH_4C_2H_3O_2$ 20% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	$Mg_2P_2O_7$ theor. gms.	P_2O_5 weight gms.	P_2O_5 theor. gms.	P_2O_5 difference	Filtrate Test
USING 0.2000 GRAM OF KH_2PO_4									
5–10	25	30	20	0.16375	0.16357	0.10445	0.10434	+0.00011	—
5–10	25	30	20	0.16331	"	0.10417	"	—0.00017	—
5–10	25	30	20	0.16346	"	0.10427	"	—0.00007	—
5–10	25	30	20	0.16345	"	0.10427	"	—0.00007	—
Average				0.16349	0.16357	0.10429	0.10434	—0.00005	
Average per cent deviation from theoretical								—0.047%	
USING 0.5000 GRAM OF KH_2PO_4									
5–10	25	30	20	0.40878	0.40899	0.26075	0.26086	—0.00011	—
5–10	25	30	20	0.40940	"	0.26115	"	+0.00029	—
5–10	25	30	20	0.40869	"	0.26070	"	—0.00016	—
5–10	25	30	20	0.40845	"	0.26055	"	—0.00031	—
5–10	25	30	20	0.40889	"	0.26082	"	—0.00004	—
Average				0.40884	0.40899	0.26079	0.26086	—0.00007	
Average per cent deviation from theoretical								—0.026%	

H_2O cc.	$NH_4C_2H_3O_2$ 20% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	$Mg_2P_2O_7$ theor. gms.	P_2O_5 weight gms.	P_2O_5 theor. gms.	P_2O_5 differ-ence	Filtrate Test
USING 1.0000 GRAM OF KH_2PO_4									
5–10	25	50	25	0.81719	0.81789	0.52127	0.52171	—0.00044	—
5–10	25	50	25	0.81823	"	0.52193	"	+0.00022	—
5–10	25	50	25	0.81848	"	0.52209	"	+0.00038	—
5–10	25	50	25	0.81802	"	0.52180	"	+0.00009	—
5–10	25	50	25	0.81836	"	0.52202	"	+0.00031	—
5–10	25	50	25	0.81918	"	0.52254	"	+0.00083	—
Average				0.81824	0.81789	0.52194	0.52171	+0.00023	
Average per cent deviation from theoretical								+0.044%	

TABLE VII-B

ANALYSES MADE DISSOLVING THE PRECIPITATE OFF THE FILTER WITH 1:3 NITRIC ACID BEFORE EVAPORATING AND IGNITING

H_2O cc.	$NH_4C_2H_3O_2$ 20% solu. cc.	Magnesia mixture cc.	NH_4OH conc. cc.	$Mg_2P_2O_7$ weight gms.	$Mg_2P_2O_7$ theor. gms.	P_2O_5 weight gms.	P_2O_5 weight gms.	P_2O_5 differ-ence	Filtrate Test
USING 0.2000 GRAM KH_2PO_4									
5–10	25	30	20	0.16219	0.16357	0.10346	0.10434	—0.00088	—
5–10	25	30	20	0.16291	"	0.10399	"	—0.00035	—
5–10	25	30	20	0.15750	"	0.10046	"	—0.00388	—
5–10	25	30	20	0.16126	"	0.10287	"	—0.00147	—
Average				0.16096	0.16357	0.10267	0.10434	—0.00167	
Average per cent deviation from theoretical								—1.626%	
USING 0.5000 GRAM KH_2PO_4									
5–10	25	30	20	0.40077	0.40895	0.25563	0.26086	—0.00523	—
5–10	25	30	20	0.40130	"	0.25599	"	—0.00487	—
5–10	25	30	20	0.40508	"	0.25939	"	—0.00247	—
5–10	25	30	20	0.40542	"	0.25863	"	—0.00223	—
5–10	25	30	20	0.40289	"	0.25699	"	—0.00387	—
Average				0.40309	0.40895	0.25714	0.26086	—0.00372	
Average per cent deviation from theoretical								—1.058%	

Summary

1. More accurate results can be obtained in the determination of P_2O_5 as $MgNH_4PO_4$ by precipitating from a solution of KH_2PO_4 rather than a solution of Na_2HPO_4.

2. Precipitation carried out in the cold under the conditions studied, is found to be incomplete while precipitation made in a hot solution using ammonium acetate is complete.

3. In igniting $MgNH_4PO_4$ to $Mg_2P_2O_7$ in a platinum crucible at a high temperature, the crucible should be protected from direct contact with the flame since the results obtained are invariably low, the amount depending upon the duration of the heating.

4. Although check results may be obtained by dissolving $MgNH_4PO_4$ in nitric acid, evaporating and igniting, it is definitely shown that there is a loss of P_2O_5 by volatilization.

5. Accurate determinations of quantitites of P_2O_5 ranging from 0.1 mgm. to 0.5 gm. can be made by washing the precipitate of $MgNH_4PO_4$ off the filter paper into a weighed platinum crucible and dissolving the small particles clinging to the walls of the beaker and remaining on the filter paper with warm dilute nitric acid. After making alkaline with ammonium hydroxide the solution is evaporated to dryness and ignited to constant weight.

6. The method developed yields results deviating from theoretical values by from 0.026 per cent to 0.047 per cent, depending upon the amount being estimated, whereas deviations of from 1.058 per cent to 1.626 per cent were obtained using the method commonly employed.

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